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Methyl tin(IV) derivatives of $HOTeF_5$ and $HN(SO_2CF_3)_2$

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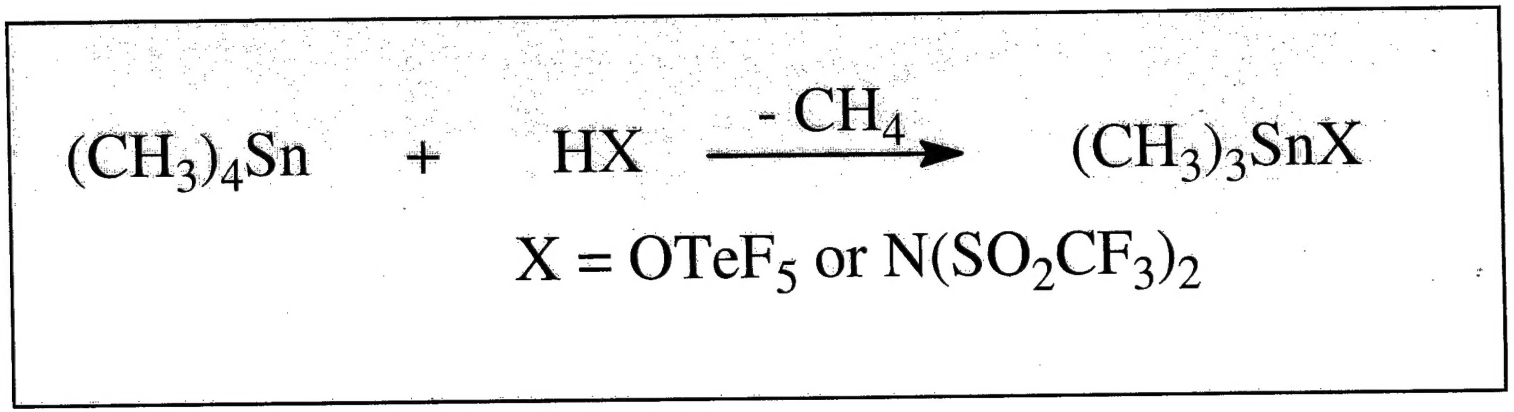
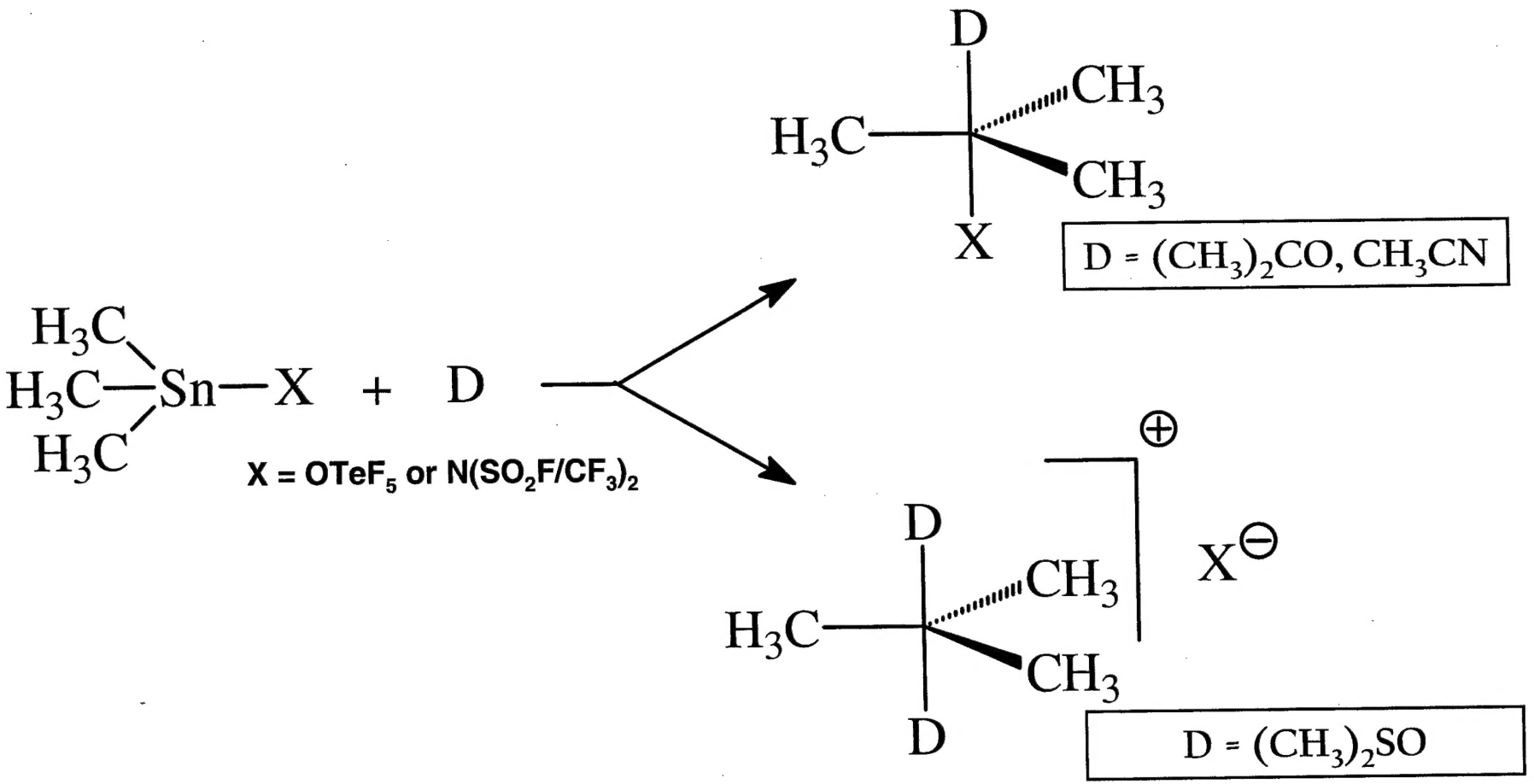
Synthesis of trimethyltin(IV) derivatives by acid solvolysis of $(CH_3)_4Sn$

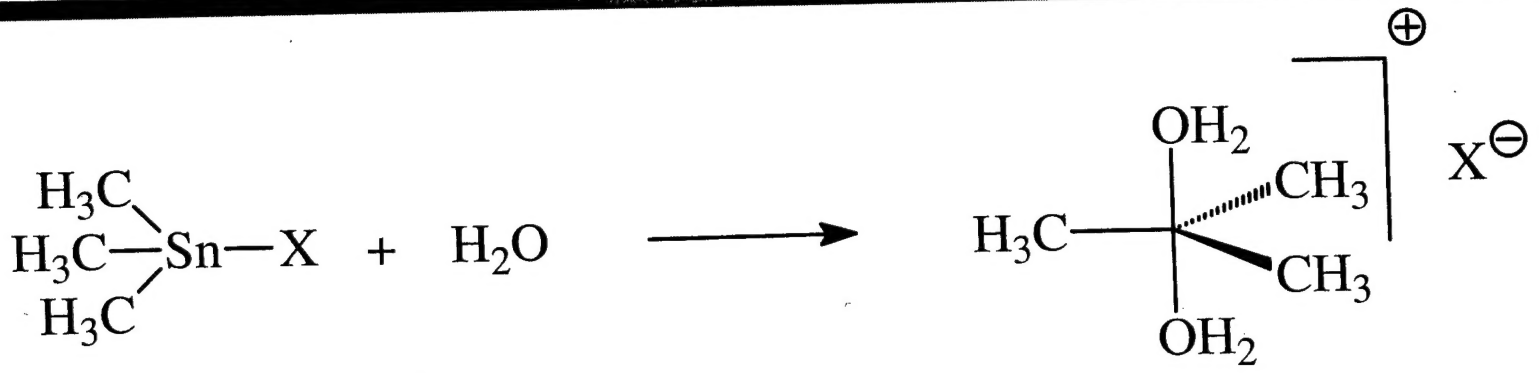


- ✓ Tetramethyltin is used in large excess
- ✓ Reaction by-products can be easily removed under vacuum
- ✓ Trialkyltin(IV) derivatives are colorless viscous oils that are highly sensitive to moisture and donor solvents.

Coordination complex formation with donor solvents



Formation of the hydrated trimethylstannyl cation



The hydrated salt can be isolated with $N(SO_2CF_3)_2$ anion but NOT for $OTeF_5$ anion.
The compound isolated is $[Me_3Sn(OH_2)_2]_2SiF_6$

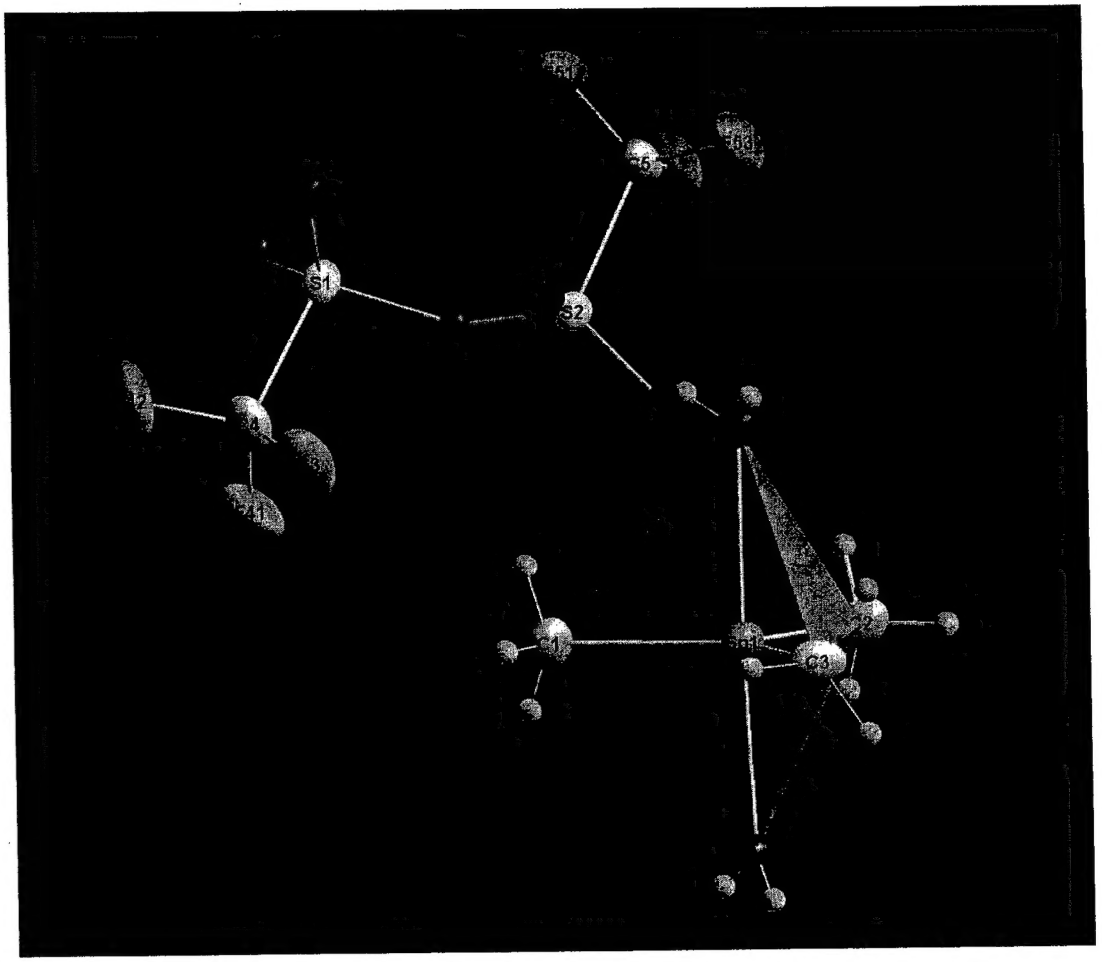
$$OTeF_5^- + 5H_2O \longrightarrow 5HF + OTe(OH)_5^-$$

$$4\,HF + SiO_2 \longrightarrow 2\,H_2O + SiF_4$$

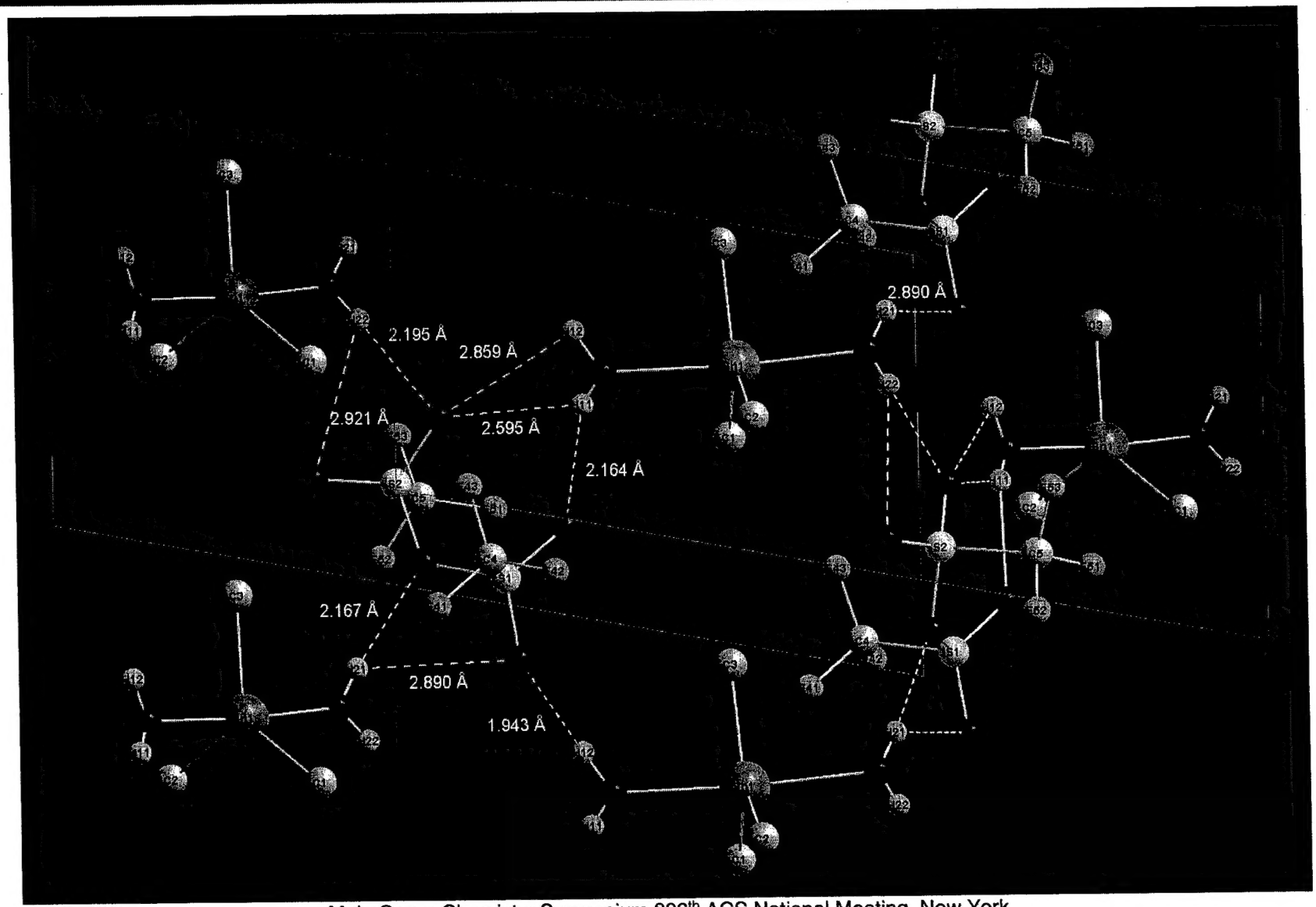
$$2F^- + SiF_4 \longrightarrow SiF_6^{2-}$$

The hydrolysis of trimethyltin teflate results in the decomposition of the $OTeF_5$ group

Hydrated trimethyltin(IV) cation



Hydrogen bonding



Multinuclear NMR Parameters

Table 1. ^{1}H, ^{13}C NMR Spectroscopic Data[a] and calculated[b,c] C-Sn-C angles for $(CH_3)_3SnX$ [X = $OTeF_5$ and $N(SO_2F/CF_3)_2$]

Solute	Solvent[d]	$\delta(^{1}H)$ ppm	$^{2}J(^{119(117)}Sn\text{-}^{1}H)$ Hz	θ(C-Sn-C)[b] (°)	$\delta(^{13}C)$ ppm	$^{1}J(^{119(117)}Sn\text{-}^{13}C)$ Hz	θ(C-Sn-C)[c] (°)
$(CH_3)_3SnOTeF_5$	neat	0.84	59.2[e]	111.7	0.84	376.9(360.3)	109.8
	CH_2Cl_2	0.79	58.5(55.9)	111.3	0.90	374.0(357.4)	109.6
	acetone	0.69	68.8(65.8)	118.8	1.55	480.4(459.3)	118.9
	CH_3CN	0.66	69.2(66.2)	119.2	1.49	484.6(463.1)	119.3
	DMSO	0.50	69.5(66.6)	119.4	1.05	511.4(490.0)	121.6
$(CH_3)_3SnOTeF_5$	AN/H_2O	0.46	69.6(66.7)	119.5	0.10	508.5(486.0)	121.4
	DMSO/H_2O	0.43	70.1(68.5)[e]	120.0	0.84	515.5(492.5)	122.0
$(CH_3)_3SnN(SO_2F)_2$	neat	0.91	63.8(61.6)	114.7	1.6	416.8(400.3)	113.3
	CH_2Cl_2	0.96	62.3(59.9)	113.6	1.4	404.1(387.7)	112.2
	DMSO	0.83	72.4(70.0)	122.2	-0.2	528.3(509.9)	123.1
$(CH_3)_3SnN(SO_2CF_3)_2$	neat	0.84	64.2(61.6)	115.0	2.1	412.6(394.1)	113.0
	CH_2Cl_2	0.81	64.4(61.8)	115.2	0.8	414.8(395.2)	113.0
	CH_3CN	0.82	70.2(67.1)	120.1	-1.7	489.5(467.6)	119.7
	DMSO	0.48	69.0(67.4)	119.0	0.7	512.2(499.0)	121.6
$[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$	CH_3CN	0.61	69.7(66.7)	119.6	0.10	491.8(470.0)	120.0
	DMSO	1.18	69.8(66.7)	119.7	0.92	512.9(497.2)	121.8

[a] NMR spectroscopic data were recorded at 300 K.
[b] Calc from relation: $\theta = 0.0161\ |^{2}J(^{119}Sn\text{-}^{1}H)|^{2} - 1.32\ |^{2}J(^{119}Sn\text{-}^{1}H)| + 133.4$.
[c] Calc from relation: $|^{1}J(^{119}Sn\text{-}^{13}C)| = 11.4\ \theta - 875$.
[d] Acetone = $(CD_3)_2CO$, DMSO = $(CD_3)_2SO$.
[e] Calculated from center of unresolved ^{119}Sn, ^{117}Sn satellites ($|J_{obs}|$ x 1.023)

NMR parameters ...continued

Table 2. ^{19}F, ^{119}Sn and ^{125}Te NMR Spectroscopic Data[a] of $(CH_3)_3SnX$ [X = $OTeF_5$ and $N(SO_2F/CF_3)_2$]

Solute	Solvent[b]	δ(^{19}F), ppm			$^2J(^{19}F_{ax}$-$^{19}F_{eq})$	δ(^{119}Sn)	δ(^{125}Te)	δ($^{13}CF_3$)	$^1J(^{125}Te$-$^{19}F)$, Hz		$^1J(^{13}C$-$^{19}F)$
		F_{ax}	F_{eq}	CF_3/SO_2F	Hz	ppm	ppm	ppm	F_{ax}	F_{eq}	Hz
$(CH_3)_3SnOTeF_5$	neat	-32.9	-41.9		182.5	270.8[c]	569.5		3112	3540	
	CH_2Cl_2	-30.3	-38.5		183.0	272.4	564.6		3188	3550	
	acetone	-29.1	-40.6		180.0	96.0	574.9		3020	3558	
	CH_3CN	-29.2	-40.8		179.0	84.2	575.0		3032	3556	
	DMSO	-16.2	-33.8		170.0	40.0	598.7		2712	3666	
$(CH_3)_3SnN(SO_2F)_2$	neat			55.5		242.5					
	CH_2Cl_2			55.6		248.6					
	DMSO			52.5		32.9					
$(CH_3)_3SnN(SO_2CF_3)_2$	neat			-78.5		240.2		118.7			320.4
	CH_2Cl_2			-78.8		251.0		118.1			319.8
	CH_3CN			-78.9		44.9		119.4			320.7
	DMSO			-78.6		37.4		120.0			321.7
$[(CH_3)_3Sn(H_2O)_2][N(SO_2CF_3)_2]$	CH_3CN			-79.0		59.0					
	DMSO			-79.1		42.8					

[a] NMR spectroscopic data were recorded at 300 K
[b] Acetone = $(CD_3)_2CO$, DMSO = $(CD_3)_2SO$
[c] ^{119}Sn NMR shows a peak at 300.7 ppm in $HOTeF_5$

Sn-C versus Sn-Cl bond cleavage

$XN(SO_2CF_3)_2$ (X = H, Cl) shows a preferential Sn-Cl bond cleavage

$$(CH_3)_3SnCl + HN(SO_2CF_3)_2 \xrightarrow{-HCl} (CH_3)_3SnN(SO_2CF_3)_2$$

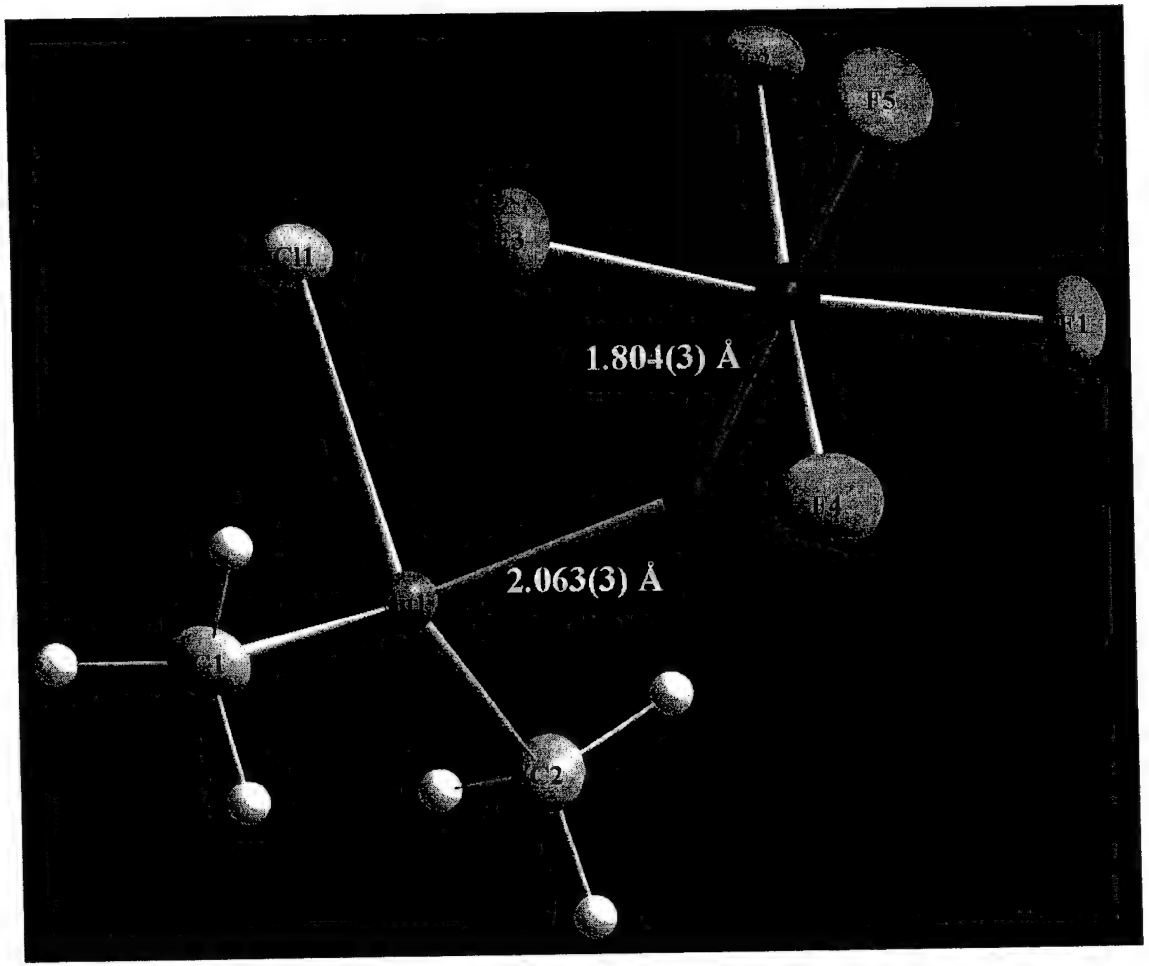
$$(CH_3)_3SnCl + ClN(SO_2CF_3)_2 \xrightarrow{-Cl_2} (CH_3)_3SnN(SO_2CF_3)_2$$

$XOTeF_5$ (X = H, Cl) shows a preferential Sn-C bond cleavage

$$(CH_3)_3SnCl + HOTeF_5 \xrightarrow{-CH_4} (CH_3)_2Sn(Cl)(OTeF_5)$$

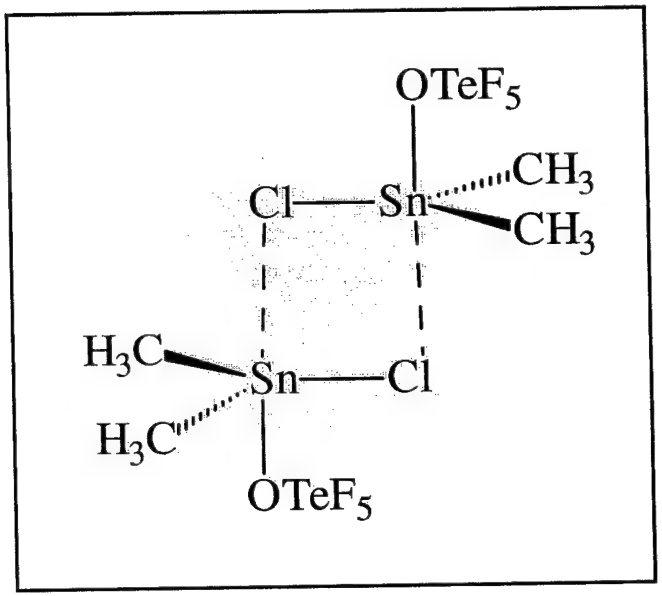
$$(CH_3)_3SnCl + ClOTeF_5 \xrightarrow{-CH_3Cl} (CH_3)_2Sn(Cl)(OTeF_5)$$

Structure of $(CH_3)_2Sn(Cl)OTeF_5$

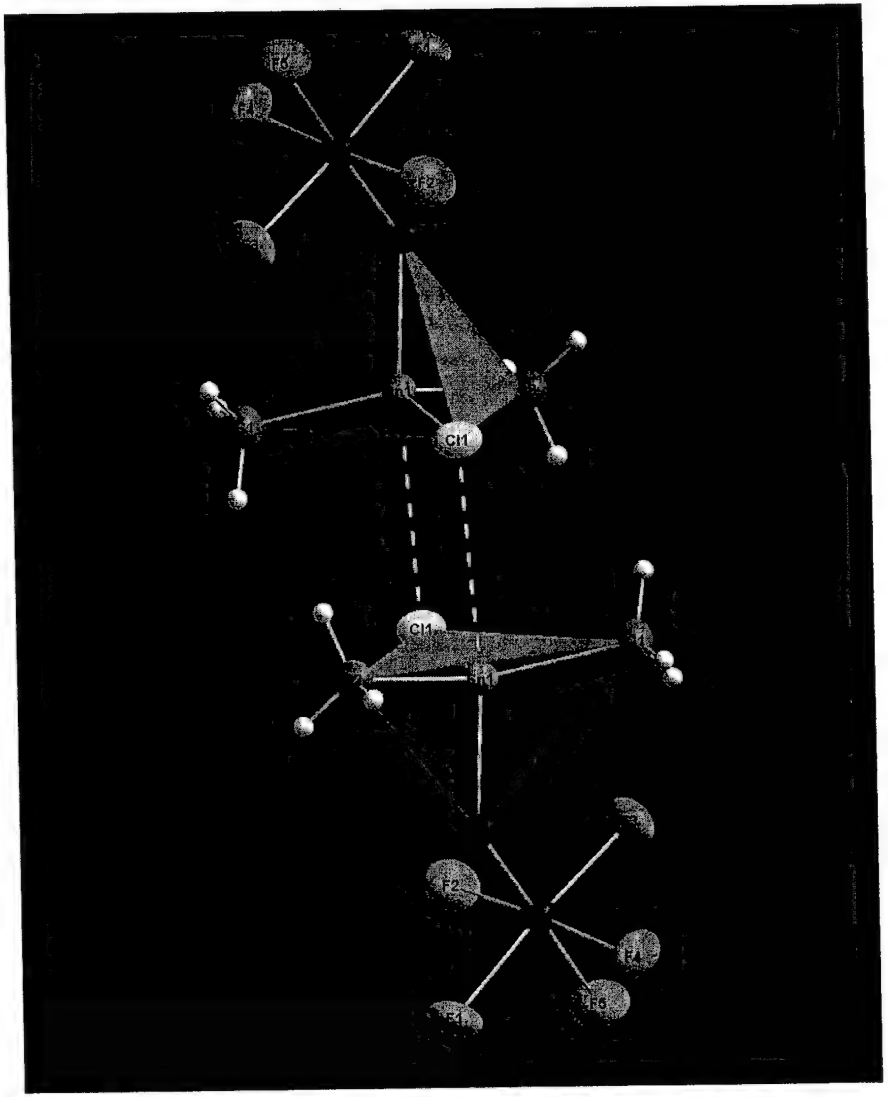


Tetra- or pentacoordinated tin???

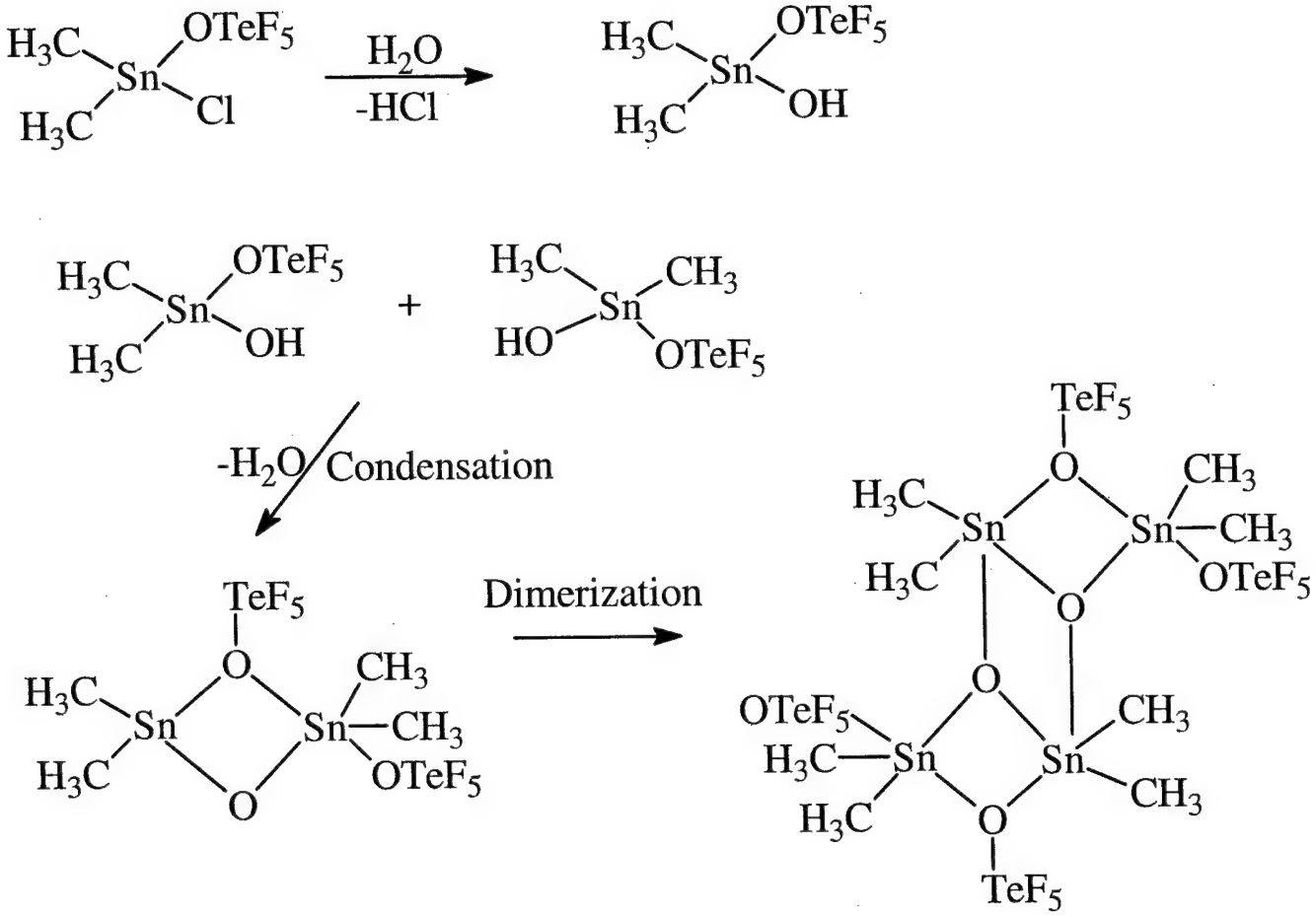
The C-Sn-C angle calculated using $^{2}J(^{119}Sn\text{-}^{1}H)$ and $^{1}J(^{119}Sn\text{-}^{13}C)$ coupling constants for $(CH_3)_2SnCl(OTeF_5)$ dissolved in CD_2Cl_2 is approximately ~118º. The $\delta(^{119}Sn)$ value of ~120 ppm indicates that tin is present in a five-coordinate environment. The fifth coordination site is most likely occupied by a bridging chlorine ligand from a second $Me_2SnCl(OTeF_5)$ molecule



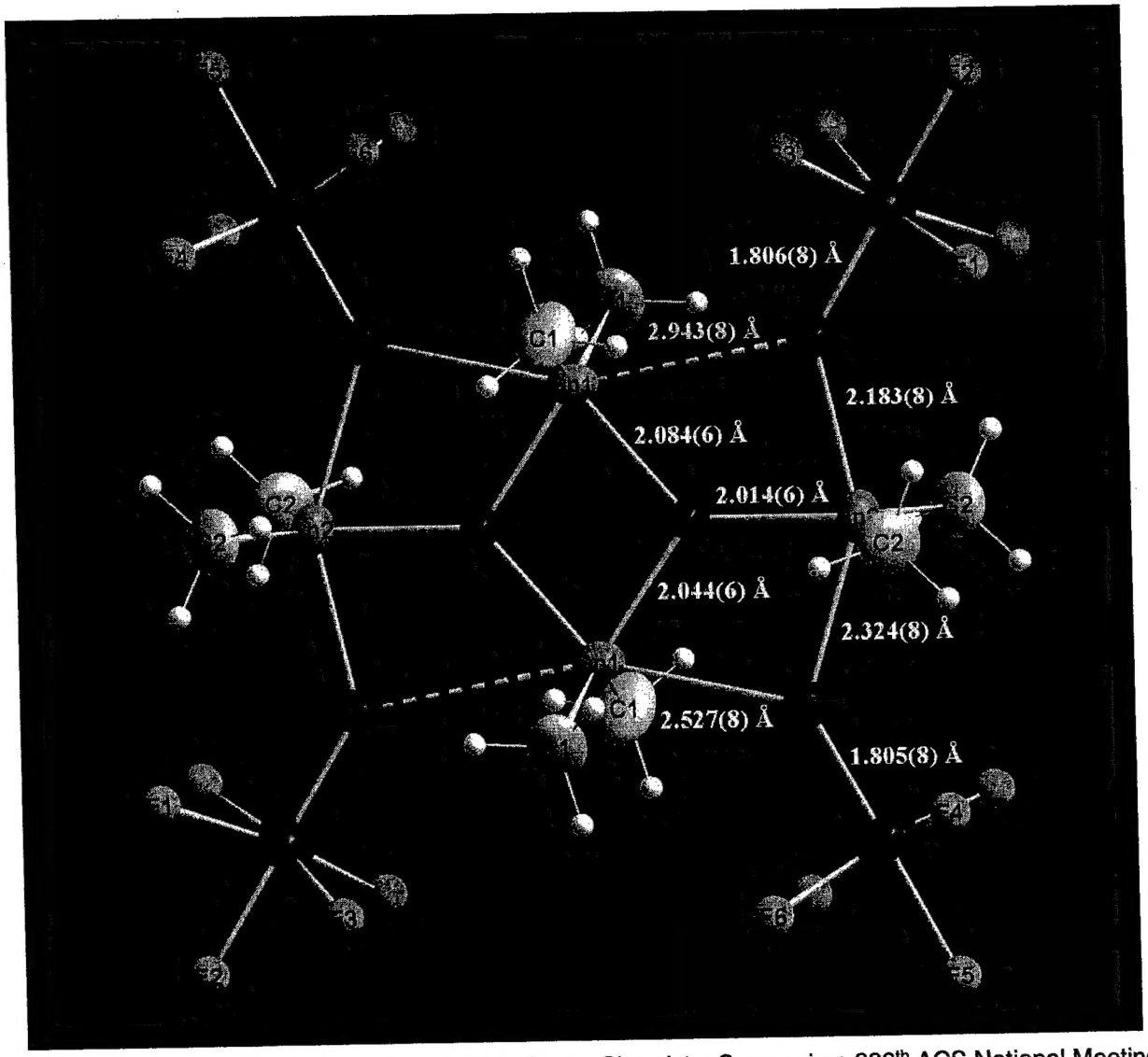
Dimerization via Sn...Cl contacts



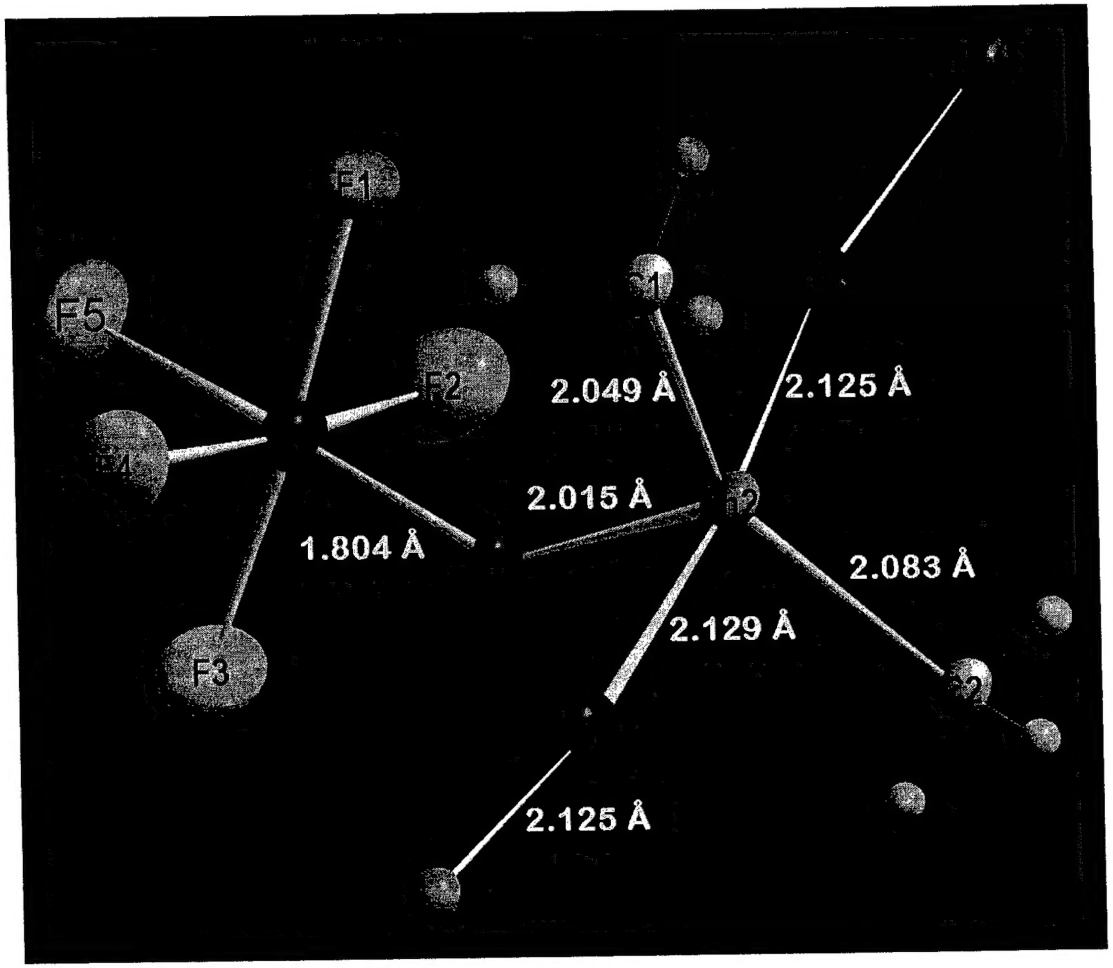
Hydrolysis of the Sn-Cl bond in $(CH_3)_2Sn(Cl)OTeF_5$



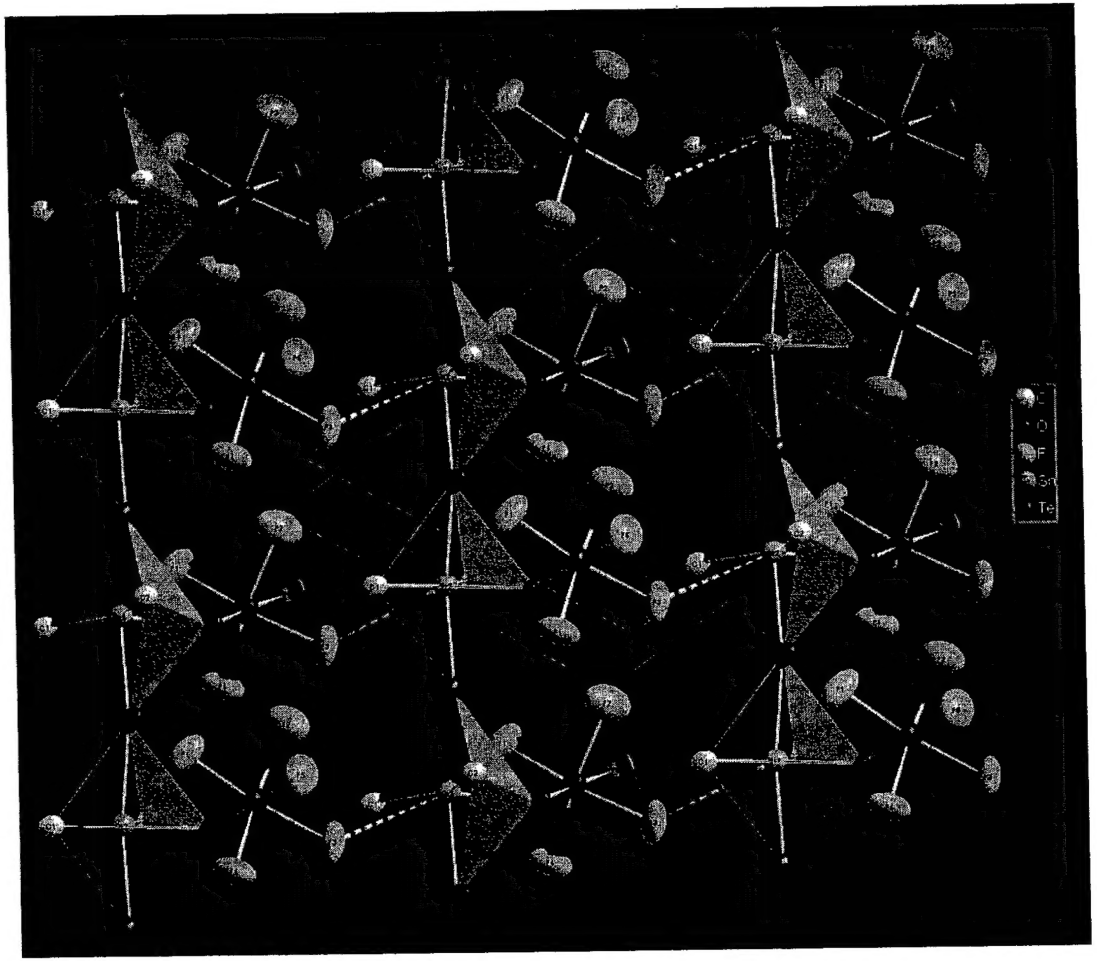
Structure of the dimethyloxotin(IV) teflate



Structure of dimethyltinooxteflate



Crystal packing showing tin and tellurium polyhedra



Conclusions

- Trimethyltin(IV) derivates can easily be prepared by the reaction of acids with excess tetramethyltin
- Trimethyltin(IV) derivatives are highly electrophilic and coordinate with solvents giving trigonal bipyramidal geometry
- In case of water and DMSO, ionic salts are formed with two donor molecules occupying the axial position
- During the solvolysis of trimethyltinchloride in $HOTeF_5$, there is a preferential cleavage of the Sn-C bond versus Sn-Cl bond
- Chlorodimethyltin(IV) teflate hydrolysizes to form a Sn-O ladder compound.
- The sublimation of dimethyltin(II) bis(teflate) results in the formation of an oxo-bridged species.